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Continental biogenic species in the Greenland Ice Core Project ice core: Tracing back the biomass history of the North American continent

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Abstract.
Ammonium, nitrate, and organic acid records from the Greenland Ice Core Project deep ice core are discussed. All species have a continental biogenic source that is situated predominantly on the North American continent for species deposited in Summit, central Greenland. The record therefore can be used to trace back the biomass history of the North American continent. Difficulty in the interpretation of these records arises from their unknown transfer behavior in a more alkaline atmosphere, which characterizes glacial time periods compared to interglacial stadials. This may have implications not only for weak acids such as formate and acetate, but also possibly for the transport and incorporation of HNO_3 into aerosols, whereas ammonium is probably not affected by the alkalinity change of the atmosphere. Our approach is to compare samples with similar H^+ concentrations throughout the record. From the records we infer several significant fluctuations in the extent of the Laurentide Ice Sheet during the last glaciation. We find evidence against the occurrence of an extensive Younger Dryas event in North America.

1. Introduction

Analysis of continental biogenic species in ice cores has potential for tracing back the history of the biomass. The methane and nitrous oxide records [*Blunier et al.*, 1995; *Chappelaz et al.*, 1993; *Leuenberger and Siegenthaler*, 1992], both species with a dominant continental biogenic source, are representative on a global scale owing to their long lifetime in the atmosphere. The main source for N_2O is the production by soil bacteria [*Cicerone*, 1989]. Methane variations are determined, to a large extent, by the expansion of low-latitude wetlands [*Blunier et al.*, 1995]. Species with a shorter turnover time will be representative of a more restricted area corresponding to the source region for a drilling site. Such species are ammonium, organic acids, and, in part, nitrate. In remote ecosystems, ammonium is produced by soil bacteria during decomposition of plants, whereafter it can be emitted from the soil solution to the atmosphere, depending on soil humidity, *p*H, and temperature. Ammonia can also be uptaken and emitted by the plant cover, depending on ambient ammonia concentration. Biomass burning is another important ammonia source, accounting for roughly one third of the ammonium deposited in central Greenland during the Holocene [*Fuhrer et al.*, 1996]. There is also a potential ocean source, which is, however, difficult to quantify [*Quinn et al.*, 1990] and is not necessarily efficient in high-latitude regions [*Silvente and Legrand*, 1993]. Organic acids as well as their precursors (i.e., various hydrocarbons) are directly emitted by vegetation [*Keene et al.*, 1995]. Emissions of organic acids from decomposing material have not, this far, been identified. Acetate also has a potential marine biogenic source [*Madronich et al.*, 1990]. Nitrate is predominantly produced by emissions of soil bacteria; however, there exist other sources such as lightning and stratospheric NO_x production (see review of *Wolff* [1995]) that may be more important for the free troposphere [*Legrand et al.*, 1989]. Long term records are available for ammonium and nitrate from Dye 3, south Greenland [*Herron and Langway Jr.*, 1985], for nitrate from Camp Century [*Herron and Langway Jr.*, 1985], and in much higher resolution for ammonium, organic acids, and nitrate at Summit, Greenland [*Legrand and De Angelis*, 1996; *Fuhrer et al.*, 1996; *Mayewski et al.*, 1994]. We will discuss the biogenic records from the Greenland Ice Core Project (GRIP) core. Since the main source region for this core is northern North America [*Fuhrer et al.*,1996; *Legrand and De Angelis*, 1996; *Whitlow*

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et al., 1994; *Davidson et al.*, 1993], these records can be related to the development of the biomass on the North American (NA) continent and further to the extension of the Laurentide Ice Sheet.

2. Discussion

2.1. Transfer Behavior With Changing Climatic Regime

For biogenic species a main interest is the variation of the source strength with time. This signal will be modulated by the atmospheric circulation system, e.g., the polar front moving back and forth, covering different source regions each time [*Mayewski et al.*,1994]. Therefore changes in source area accounting for the deposition of chemical species in Greenland have to be distinguished from changes in source strength of a specific region. Further, the signal of the source strength reaching Greenland will be affected during the transport for different climate regimes owing to different scavenging during transport and/or dilution of concentrations with changing accumulation rates. Also, a change in alkalinity and aerosol content of the atmosphere will modulate the signal by affecting the incorporation into the liquid/solid phase.

To infer local atmospheric concentrations over Greenland, we can compare fluxes of chemical species to accumulation rates. A simple model approach suggests a linear relationship if scavenging is proportional to the atmospheric concentration. From preindustrial ice core data, *Legrand and Delmas* [1988] conclude that deposition processes can be roughly described by the simple model $c_{ice} = k_1 \times c_{atm} + k_2 \times c_{atm}/acc$ [*Legrand*, 1995], where k_1 and k_2 describe the wet and the dry deposition, respectively; c_{ice} is the concentration of the chemical species in the ice; c_{atm} is the concentration in the atmosphere; and acc is the yearly accumulation rate. Also, NO_3^- Holocene values (see review of *Wolff* [1995]) seem to fit such an equation (Figure 1). Thus efficient scavenging (which would also render the first term inversely proportional to the atmospheric concentration) seems not to be important for these low accumulation sites. Since the strong acids are expected to be uptaken efficiently into cloud water, the fact that no dilution effect is observed with increasing accumulation rate could imply that the sites differ only in frequency of precipitation events.

Often, fluxes are used instead of concentrations to account for the changing accumulation rate with changing climate. As seen from the above fit, this approach is only valid if dry deposition dominates the deposition to the ice sheet. On the basis of this model the contribution of dry deposition to, e.g., ammonium, does not exceed 40% during the whole climatic cycle, starting with an estimate of today's dry-deposition contribution of 10% [*Bergin et al.*, 1995]. Fluxes will therefore not give a better picture of the atmospheric concentration above Summit. A further limitation of this model arises from the assumption of constant k_1 and k_2 with changing climates. The subject is not conclusive. *Cunningham and Waddington* [1993] suggest an increased k_1 with cold periods due to enhanced ventilation, but there is also evidence for constant k_1 and k_2 in cold and warm stages [*Legrand*, 1985].

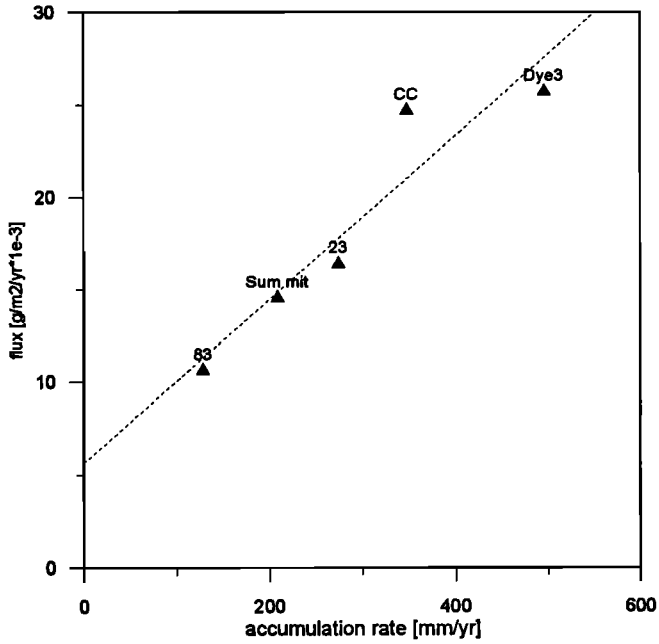

Figure 1. Preindustrial nitrate fluxes (concentrations x accumulation rates) plotted against yearly accumulation rates from sites in Greenland, summarized by *Wolff* [1995].

This approach, either using fluxes or a correction based on the linear fit as shown in Figure 1, gives insight only into the potential local atmospheric concentration. To assess the processes occurring during the transport from the source region, the dependence of concentrations on *p*H is considered in Figure 2. Samples were selected from the period of the last glacial maximum between 1800 and 2046 m as proposed by *Legrand and De Angelis* [1996], who assumed an unchanged source strength based glaciation history on the North American continent. *Legrand and De Angelis* [1996] suggest that the increase of formate concentration with increased alkalinity is due to the changed incorporation process into cloud water. We point out that this fit would then describe the net effect of an alkaline atmosphere on transport and deposition of this species. A correction for this effect will not yield the local atmospheric concentration but rather the source strength. It is also possible that changes in atmospheric circulation strength are implicitly included in the fit. Applying this correction to the whole data set assumes that this fit remained the same throughout the whole record. In view of the changing distribution of sources of strong acids, weak acids, and bases with the changing extent of the ice sheets and changing sea level during the last glaciation, this is not necessarily the case. Further, since ammonium plotted versus *p*H suggests a slope of the same sign as for formate (Figure 2), though with a weaker correlation, it is likely that incorporation processes due to the more alkaline atmosphere do not dominate the correlation bet-

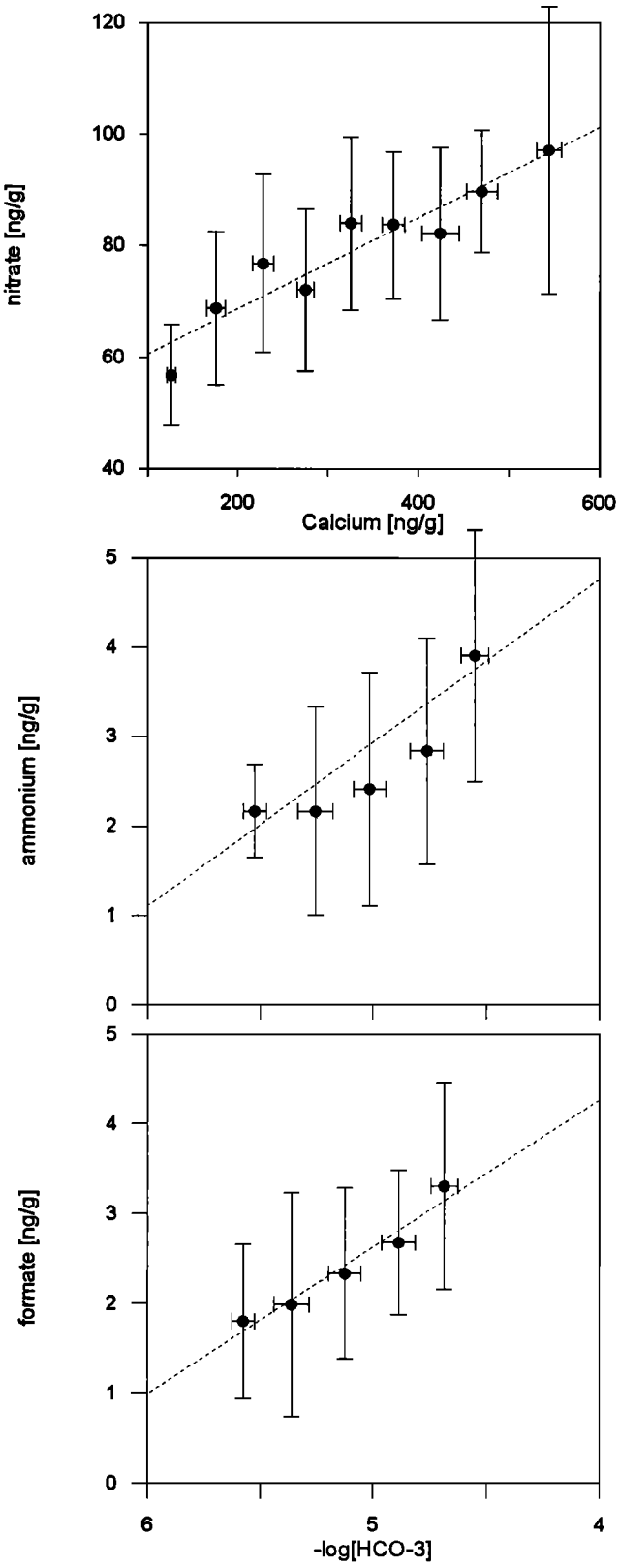

Figure 2. Formate and ammonium concentration from the last glacial maximum (1800 to 2046 m; samples from interstadials are excluded) plotted against the *p*H of the sample (HCO_3^- concentrations correspond to the negative H^+ concentrations that are calculated from the ion balance [*Legrand and De Angelis*, 1996]). Nitrate is plotted against the Ca^{2+} concentration.

ween concentrations and *p*H. Transport and deposition of ammonia, which is a strong base, would be affected in the opposite way to formate. To rely on the corrected record seems very shaky when one cannot discern the processes at play for which the correction would be valid. A more direct approach arises from the comparison of samples with the same *p*H. Figure 3 shows an overview of the records for H^+ concentrations between 0 and 1 ng/g and between 1 and 3 ng/g. For nitrate, instead of H^+, the Ca^{2+} concentration is used as a selection criterion (Figure 2) since an efficient uptake of nitric acid occurs with alkaline particles. (HNO_3 as a strong acid would not be affected by the *p*H of cloud water). Again, we point out that in the case of a changed distribution of sources or atmospheric circulation, the change in concentration between glacial and Holocene samples cannot be directly related to a change in source strength.

In Figure 4 the *p*H-corrected and uncorrected records are presented.

2.2. Most Recent Deglaciation

To get a picture of the timing of the species following a climate change, we first investigate the most recent transition from the last glacial age into the present warm stage. Figure 5 shows an overview of biogenic species over the last 18,000 years. Ammonium starts to increase slightly around 17,000 years, reaching the maximum concentration of the the last 130,000 years during the Younger Dryas (YD) cold period between 12,700 and 11,550 years B.P. Formate shows a first small increase at the transition from the last glacial into the Allerød Bølling (AB), remains unchanged during the YD, and increases again at the transition into the preboreal. However, unlike for ammonium a further increase of a factor of 2 is observed during the first part of the Holocene [*Legrand and De Angelis*, 1995]. Acetate shows low glacial values until around 9000 years B.P., whereafter it recovers quickly to Holocene concentration at around 8000 years B.P. [*Legrand and De Angelis*, 1995]. Nitrate also increases before the AB transition and shows maximum concentrations during the YD [see *Mayewski et al.*, 1994], followed by a decreasing trend throughout the Holocene. Both ammonium and formate change drastically by a factor 5 to 10 from low glacial values to maximum Holocene concentrations, whereas acetate and nitrate show an increase by only a factor of 2 and less. We suggest the following hypothesis: Immediately after the Laurentide Ice Sheet began to retreat after the glacial maximum at around 18,000 years B.P., no organic material was available that could produce ammonia through decomposition. The vegetation once covered by the glacier was outwashed or covered by large amounts of erosion material. The high concentrations reached in the Younger Dryas and the early Holocene may be due to ecosystems that live mainly on N_2 fixation being more adaptive during this time period because of the poor availability of organic material. This is in contrast to more elevated biomes such as boreal forests, which are also adapted to uptake am-

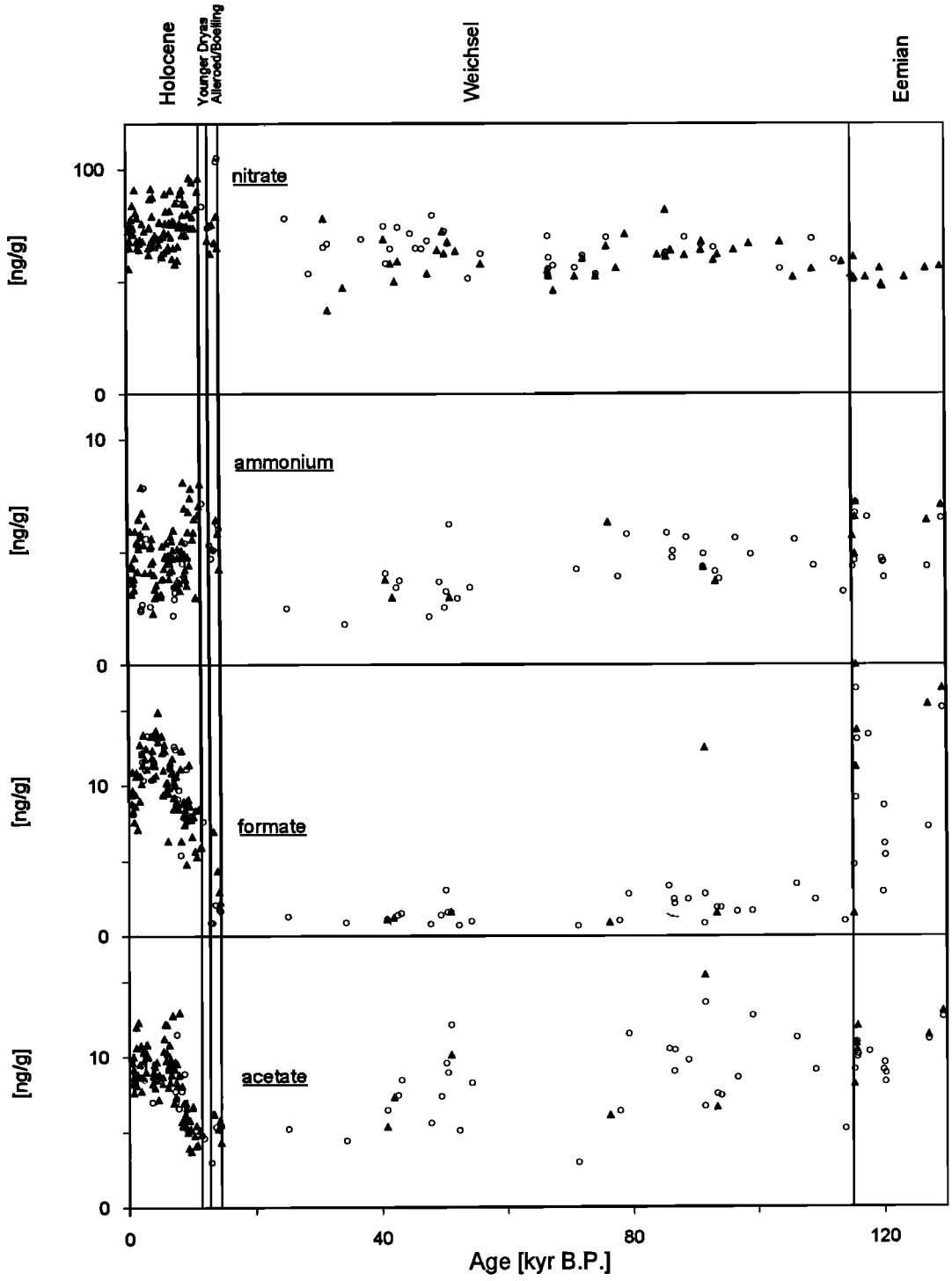

Figure 3. Ammonium, formate, and acetate concentrations of acidic samples from the last climatic cycle (samples with biomass burning events or volcanic events, which would affect the *p*H of the samples, are excluded from the data set). Circles indicate samples with an H^+ concentration between 0 and 1 ng/g; triangles denote concentrations between 1 and 3 ng/g. Nitrate concentrations are plotted for Ca^{2+} concentrations between 0 and 1 ng/g (triangles) and between 1 and 2 ng/g (circles).

monia that is emitted from soils or directly through the root system. This change in vegetation cover after the transition into the Holocene may cause the decreasing trend observed with ammonium. The decrease that is observed for ammonium throughout the Holocene and, later on, also for formate was suggested to be due to the temperature decrease that followed the decreasing solar radiation after the last maximum in 60°N at 9000 B.P. [*Fuhrer et al.*, 1996]. This causality is also supported by the strong covariation of the ammonium record with

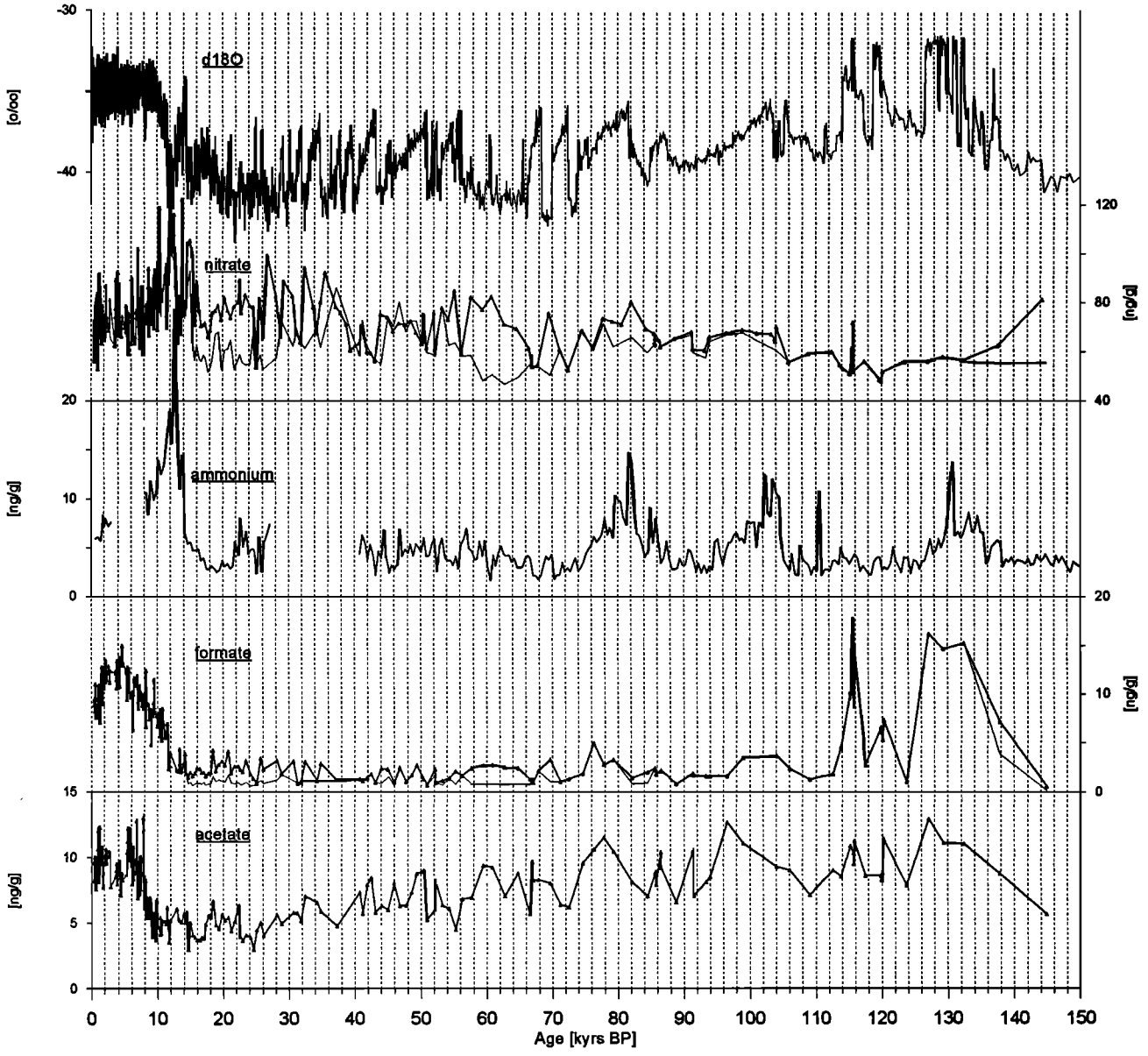

Figure 4. Overview of biogenic species from the Greenland Ice Core Project (GRIP) core. Ammonium is measured continuously; formate, acetate, and nitrate are analyzed by ion chromatography on single samples. For formate and acetate, only background concentrations are shown (samples with biomass burning events or volcanic events, which would affect the *p*H of the samples, are excluded from the data set). For nitrate and formate, curves corrected for alkalinity are added (thin lines). The $\delta^{18}O$ record (top) is from *Dansgaard et al.* [1993].

the solar radiation at 60°N over the last climatic cycle [*Meeker et al.*, this issue]. The same effect could be responsible for the decrease in nitrate concentration in the early Holocene. The delayed response of formate and acetate to the transition may be explained by the time needed to evolve for the vegetation type that emits organic acids or their precursors.

The lag of acetate compared to formate may be due to a shorter lifetime, which results in acetate reaching Greenland only when the Laurentide Ice Sheet had retreated to the east. It is not conclusive if the rise in acetate is related to the Hudson Bay lowlands becoming ice free since the timing is still controversial [*Mayewski et al.*, 1981; *Peltier*, 1994]. *Legrand et al.* [this issue] suggest that the delay in acetate is possibly caused by marine biogenic emissions that were depressed at the beginning of the Holocene because of melting continental ice. This was suggested based on low methanesulfonate (MSA) values found during this period. MSA is a good tracer of marine biogenic production. The dominating influence of noncontinental sources would explain the minor changes in concentration between the last glacial maximum and the Holocene for acetate and nitrate (for which lightning and stratospheric N_2O oxidation may be important), whereas low formate and ammonium values during the last glacial maximum (Fi-

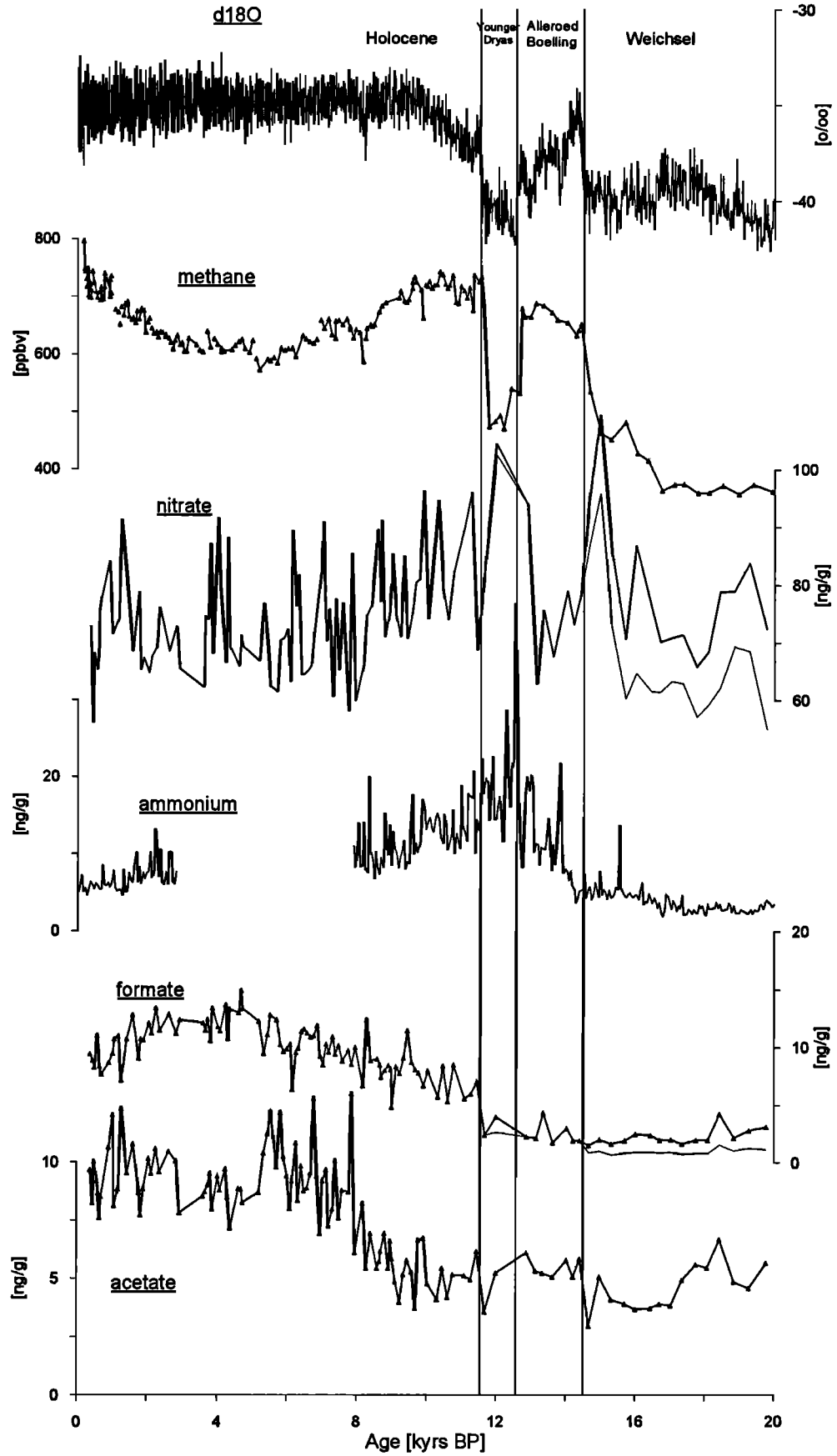

Figure 5. Overview of biogenic species from the GRIP core for the last deglaciation and the Holocene. Curves corrected for the alkalinity and the Ca^{2+} concentration, respectively, (see text) are added for formate and nitrate (thin lines). Methane is taken from *Blunier et al.* [1995].

gure 4) support a mainly continental biogenic origin for these species. Assuming that the transfer behavior for nitrate remained unchanged for the samples selected in Figure 4, we conclude that atmospheric ice age concentration above Summit was lower by about 20%. Assuming further that soil emissions are the only source for nitrate that is affected by a climatic change (contrary to lightning and stratospheric input) and that nitrate originating from a soil source would have changed proportionally to ammonium, i.e., by about a factor of 2-3 between the glacial and mean Holocene concentrations, we estimate that the contribution to nitrate deposited on the ice sheet during Holocene is about 30%. This value is in good agreement with the estimate of 25% made by *Wolff* [1995]. The fact that this estimate is lower than the contribution of HNO_3 soil emissions to the global budget of natural HNO_3 emissions, where soil emissions dominate [*Wolff*, 1995], may be due the easier access to the free troposphere for sources like lightning and stratospheric production compared to surface sources. The estimate suggests that the seasonality of nitrate [see, e.g., *Steffensen* 1988], which involves up to 50% of the nitrate concentration is not only caused by the seasonality of biogenic source strength, but also is probably due to a seasonality in the transport pattern. A change of lightning frequency during glacial times cannot be assessed here. As far as stratospheric production of nitrate is concerned, an increase of stratospheric ozone was suggested by *Staffelbach et al.* [1991] and decrease of N_2 was measured by *Leuenberger and Siegenthaler* [1992]. This would imply a decrease of NO_x production. The extent to which this affects tropospheric NO_x concentrations has to be estimated by model calculation. In any case our estimate for soil contribution becomes an upper limit.

2.3. Glaciation History of the Laurentide Ice Sheet

The very low ammonium concentrations between 18 and 22 kyr B.P. coincide with the time of the maximum extent of the Laurentide Ice Sheet when the source area for ammonium was ice covered. The glaciation history of the Laurentide Ice Sheet during the Wisconsin is still under discussion. On the basis of amino acid ratios, *Andrews et al.* [1983] propose several deglaciation stages for the Hudson Bay lowlands, i.e., 35, 65, 85, and 105 kyr B.P. In roughly the same time intervals, lows in sea surface temperature are derived from sediment cores in the North Atlantic, and these are related to meltwater input from the southern margin of the Laurentide Ice Sheet and to the 23 kyr precessional cycle [*Ruddiman and McIntyre*, 1981]. *Boulton and Clark* [1990] infer from glacial lineations a single continuous period of deglaciation of the Hudson Bay lowlands between 80 and 40 kyr B.P. A review by *Clark et al.* [1993] suggests that the Hudson Bay lowlands became ice free in stage 5a and possibly remained ice free during stages 4 and 3. However, the authors point out that owing to dating uncertainties, a glaciation of the Hudson Bay lowlands during stage 3 and possibly stage 4 is also likely. Major advances of the southern margin occurred in stage 4 and again in stage 3, whereafter it reached its maximum extent in stage 2. Going back in time, we find several periods with ammonium concentrations as low as during the last glacial maximum (see section 2.2), i.e., between 105 to 124 kyr B.P., between 86 and 92 kyr B.P., and between 64 and 74 kyr B.P. As was discussed concerning the transition into the present interglacial, ammonium concentrations follow immediately the buildup of biomass with the retreat of the ice sheet. We therefore suggest that these intervals with low ammonium values support the existence of several strong fluctuations in the extent of the Laurentide Ice Sheet [*Fuhrer et al.*, 1996]. The fact that formate concentrations do not recover during the whole glacial period may be due to a climate that is unfavorable to a vegetation which emits formate. As observed previously, formate emissions are considerably delayed with the transition into the Holocene. This lag may be increased with large parts of the ice sheet persisting also during the periods of deglaciation [*Clark et al.*, 1993]. The high acetate concentration throughout the early Weichsel may therefore not be due to an extensive continuous deglaciation of the Hudson Bay lowlands. We point out that biased sampling may lead to an overestimate of average acetate concentrations. As shown in Figure 6, samples from the discussed intervals of the discontinuous record compared with the continuous record show higher than average levels of ammonium and potentially also of acetate, if its source is mainly of continental biogenic origin.

2.4. Occurrence of a Younger Dryas Event in North America

The occurrence of a Younger Dryas event in North America is still under debate. A cold period around 11,000 years B.P. could be confirmed from pollen records for the east coast [*Peteet et al.*, 1993; *Mott and Stea*, 1993]; however, the results from the interior continent are not conclusive. This is due to dating uncertainties, on one hand, and to the difficulty with pollen records to separate influences of the local climate from regional representative features, on the other hand. For example, evidence of a cold event was found in the midwest region of the United States [*Shane and Anderson*, 1993], but the idea that it was only a regional phenomenon, linked to drainage events from the Great Lakes, could not be excluded. The difficulty in dating arises from ^{14}C plateaus in this time period [*Lotter*, 1991]. GRIP ice core records, which are well dated and where no sources are in close vicinity for continental biogenic species, may therefore contribute to the discussion. We find the highest ammonium concentration of the whole record during the Younger Dryas interval. This invites the arguments that ammonia emissions in NA were not reduced during YD and a cold event did not take place during that time period. However, we have to take in account possible changes in the transfer function. Such changes are very obvious, e.g., in Interstadials 3 and 4 (about 25 kyr B.P.), where ammonium concentrations dropped by 50% during 200 to 300 years. We assumed,

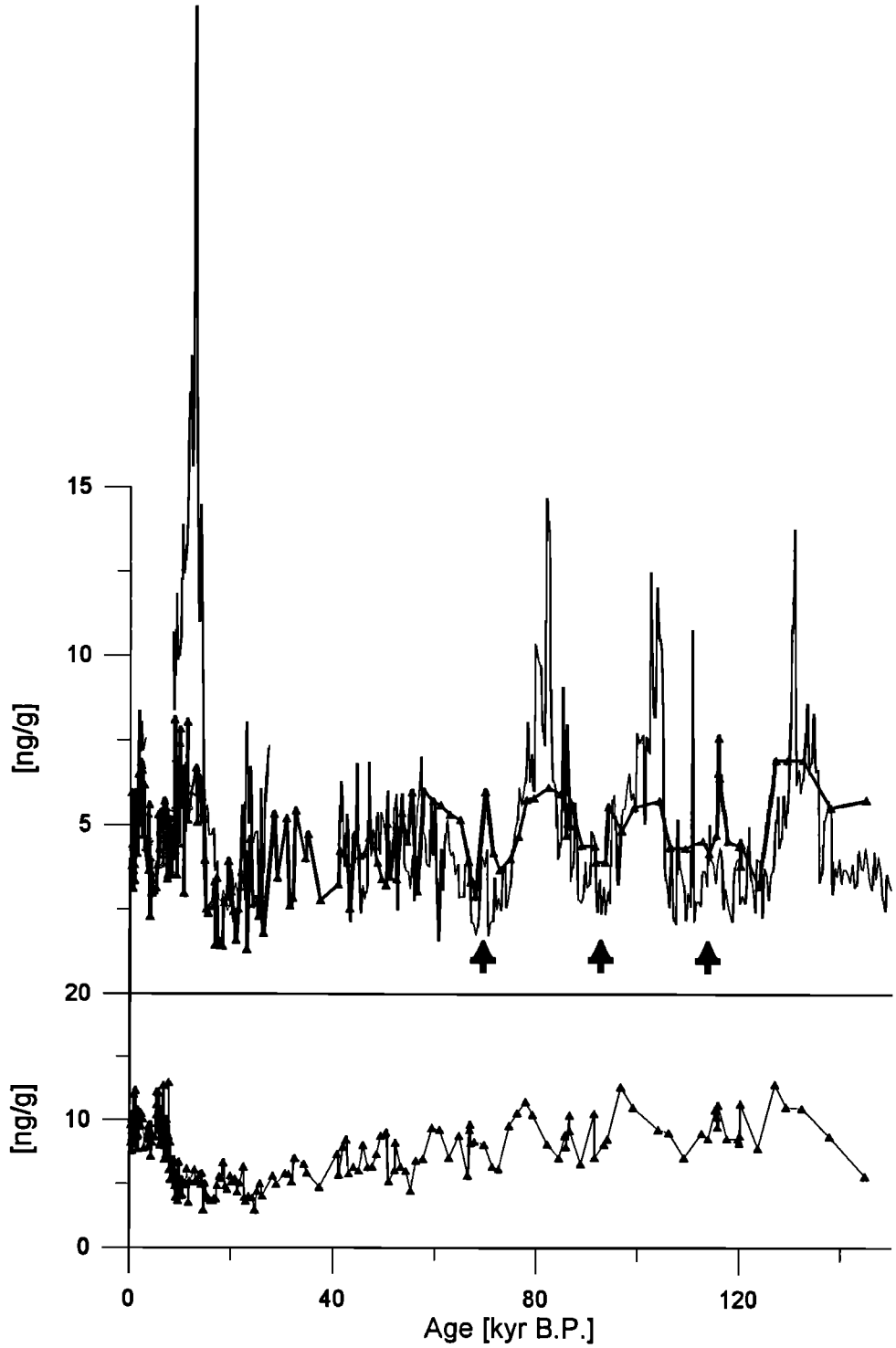

Figure 6. Comparison of ammonium measured continuously with continuous flow analysis and ammonium analyzed on single samples with ion chromatography. Acetate measured on the same samples is added to point out intervals with potentially too high concentrations compared with the average level (see arrows). (Samples with biomass burning or volcanic events are excluded from the discontinuous records).

for this time period, an unchanged source strength for ammonium and therefore ascribe this drop to changes in transport and deposition efficiencies and/or changes in transport path, e.g., changes in the extension of the polar cell [*Mayewski et al.*, 1994]. Since the latter influence would diminish with the retreat of the Laurentide Ice Sheet, we consider, for the following discussion, this factor 2 change in concentration as an upper limit for possible changes of the transfer behavior of adjacent climatic stages during the deglaciation period.

Contrary to the glacial stage, changes in concentration are not as clearly linked to climate changes during the most recent climatic changes from the Oldest Dryas into the Holocene since a change in ammonia source strength is overlayed. No change in mean concentration is observed between the 200 years before and after the transition into the AB. So (1) either changes in transport and deposition mechanisms do not dominate at this stage or (2) their decreased efficiency is compensated by an increase in ammonia emissions caused by the buildup of biomass. Most chemical species (except ammonium and nitrate) show similar concentrations in the Younger Dryas and in the Allerød Bølling [*Mayewski et al.*, 1993]. We assume also that transport and deposition parameters were similar in both time periods. For the transition into the YD we would therefore expect the opposite behavior to the transition into the AB. If scenario 1 were true, we would expect no change in concentration for the time periods just before and after the transition; but roughly a 100% increase is observed between the 200 years before and after the transition into the Younger Dryas. This would imply an increase in source strength. If scenario 2 were true, the question arises of which ammonia emissions occur after a deterioriation in the climate regime in the source region, i.e., if increased ammonia emissions could occur with decomposition of plant material. An increase would be difficult to prove from the data record, without quantitative knowledge of the transfer behavior since it would always be overlapped by enhanced transport and deposition mechanisms. It is easier to find support for the opposite occurrence; for example, in marine isotopic stage 5 we find a cold stage (between Interstadials 22 and 23 at about 84 kyr B.P.), where a clear drop in ammonium concentration is observed [see *Fuhrer et al.*, 1996]. The $\delta^{18}O$ and Ca^{2+} levels are similar as in YD as well as the ammonium source strength obviously recovered already in the preceeding warm stage (like in AB). Since all other factors tend to increase the ammonium concentration in a cold stage, we have to assume that ammonia emissions in the source region are severely affected by this cold event. There is no evidence for a dominating effect of ammonia emissions from decomposing plant material. Taking this situation as representative for a cold event affecting the source region, scenario 2 suggests that no extensive cold event took place in the ammonium source region and the increase is caused by the usual change in transport and deposition mechanisms. For a safe conclusion on the occurrence of a cold Younger Dryas event in North America, a greater knowledge of the transfer function is certainly required.

2.5. Biomass Burning History of North America

All biogenic species mentioned above are also emitted by biomass burning. Biomass burning has an impact on the oxidation capacity of the atmosphere and on tropospheric trace gas concentrations [*Cofer et al.*, 1991; *Rodriguez et al.*, 1991]. Further, a record of past fire frequency would also give insight into the prevalent climatic conditions.

The fingerprint of high-latitude biomass burning events could be identified by its chemical composition in the GRIP ice core [*Legrand et al.*, 1992]. Whereas only a minor enhancement is observed in nitrate and acetate, formate and ammonium are found in an almost stoichiometric ratio during the Holocene, with concentrations up to 100 times the background level. Biomass burning contributes 20% to 30% to the ammonium deposited in central Greenland during the Holocene [*Fuhrer et al.*, 1996]. For formate a similar estimate was made by *Legrand and De Angelis* [1996] for the last 200 years. Also, significantly enhanced H_2O_2 and HCHO levels often go along with biomass burning events recorded in the ice [*Fuhrer et al.*, 1993]. These species are directly related to the oxidation capacity of the atmosphere [*Thompson*, 1995]. The biomass burning contribution for these species is more difficult to estimate since their concentrations are smoothed out after deposition owing to strong interaction with the gas phase. An estimate of their contribution has still to be established. On the basis of the formate-ammonium correlation a threshold value could be derived for ammonium originating from biomass burning, at least for the Holocene epoch [*Fuhrer et al.*, 1996; *Legrand and De Angelis*, 1996].

A decreasing trend of biomass burning ammonium was inferred during the Holocene, in agreement with the trend in charcoal sediments found in Canada [*Fuhrer et al.*, 1996; *Terasmae and Weeks*, 1979; *Anderson et al.*, 1989]. This correlation illustrates that biomass burning events recorded in ice cores offer a new tool to trace back the fire frequency of NA. However, assumptions on the meteorological conditions have to be made, for the recording of a fire in Greenland depends on the transport path of the biomass burning plume. So far, only sharp events could be identified in the ice, and a possible contribution of biomass burning to the "background" levels of these species could not be evaluated. Biomass burning events were also found in glacial times, in both cold and mild stages. To expand the record of fire frequency into the past, a threshold value has to be derived from higher-resolution formate measurements.

3. Conclusions

Now that the Summit ice core chronology is well established, the analysis of continental biogenic species offers the possibility of precisely dating variations in the vegetation history, which were beyond the dating resolutions of other paleoenvironmental records. Since the main source region for biogenic species with a short turnover time is the NA continent, we infer from our records the glaciation history of the Laurentide Ice Sheet during the early Wisconsin. Our data provide evidence for several strong fluctuations in the extent of the ice sheet during the last glaciation. Further, we infer that no extensive cold period took place on the NA continent during the Younger Dryas period. The timing of the concentration changes of the different biogenic spe-

cies during the last deglaciation gives insight into the favorable conditions for the emission of these species in their source areas, though a better understanding of the corresponding emission rates above different natural ecosystems has to be acquired to confirm the hypotheses. Currently, available data are not sufficient for a detailed analysis of the causes of the variations in concentrations. We point out that a further evaluation of the presented ice core records will also require a better understanding of the transfer behavior of these species in a changing climatic regime. Studies of the incorporation processes for the solid and liquid phases are needed as well as circulation models that include homogenous and heterogenous chemistry. Without such an approach, only the above presented qualitative interpretation is accessible.

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